Indian J. Phys. **68A** (5), 459 – 464 (1994)

IJP A
- an international journal

Photoacoustic study of Nd and Er ions doped in calibo glass

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Received 8 March 1994, accepted 7 June 1994

Abstract : The photoacoustic spectra of Nd and Er ions doped in calibo glass have been recorded in the 400–800 nm using an indigenous single beam photoacoustic spectrometer. It has been found that the photoacoustic signal attributed to the rare-earth ions is strong in the oxide and become very weak when these ions are placed in the host lattice calibo glass The assignment of the peaks in the calibo glass shows a red-shift in their spectra as compared to their position in the free ions The PA branching ratio have also been determined which may be useful in understanding the mechanism of laser action.

Keywords : Photoacoustic spectroscopy, PA branching ratio, relative intensity, non radiative, doped glasses

PACS Nos. : 82.80.Kq, 78.66.Jg

1. Introduction

The photoacoustic technique has recently been revived as a spectroscopic tool for the study of solid, liquid and semi-solid material, which are difficult to investigate by means of conventional absorption and reflection technique. The photoacoustic effect arises when intensity modulated light is absorbed by a sample inside an airtight gas-filled chamber. Periodically deposited heat in the sample is transferred to the gas by thermal conduction and this causes pressure fluctuation in the gas at the modulation frequency. The pressure oscillation is detected by a microphone, and this constitutes the photoacoustic signal.

In the present paper, we report the photoacoustic spectra of Nd and Er doped in calibo glass. In this type of materials, many investigations [1–5] have recently been carried out by absorption fluorescence and photoacoustic technique because of their uses as interesting laser materials. The trivalent rare-earth ions offer many possibilities for stimulated emission because they have large number of energy levels in every region of the visible and near-infrared portions of the electromagnetic spectrum. The lasing characteristics are essentially determined by the electronic energy levels of the rare-earth ions and presence of the other ions in the vicinity, may have considerable influence on them. It has therefore, become increasingly interesting to study the absorption and luminescence characteristics of glasses doped with rare-earth ions. Molecular excitation followed by the fluorescence is beset with an inherent limitation in that level which have long, radiative life time usually giving very weak fluorescence and are difficult to detect. Since these levels may be controlling ones as far as the population inversion for laser action is concerned, their identification and characterization by other means are desirable.

2. Experimental

2.1. *Material preparation :*

Rare-earth doped calibo glasses for our study were prepared by melting a mixture of calcium oxide, lithium oxide, boric oxide and rare-earth ion in its elemental powder form, in platinum crucible at 1100°C for about five hours and pouring the melts into a suitable cast. The compound CaO, Li_2O_3 and B_2O_3 were obtained from BDH with a stated purity of 99% and rare-earth powders were obtained from Aldrich company and had stated purity of 99.9%. The weight percentages were 20% CaO, 10% Li_2O_3, 70% B_2O_3 and 4% of required rare-earth ion. The glasses were cast in stainless steel disc of about 10 mm diameter and 5 1 mm thickness the disc were annealed at 350°C for one hour to reduce the strain in the glass.

2.2. *Recording of photoacoustic spectra :*

The photoacoustic spectra of the glasses in the 400–800 nm region have been recorded by using a single beam photoacoustic spectrometer [6]. The light beam from a 600 Watt tungsten halogen lamp dispersed by a 0.25 m grating monochromator with slit width 2 mm (7 nm band width) and chopped at 22.5 Hz was allowed to fall on sample. The signal thus obtained was amplified and fed to the Look-in amplifier (EG & G model 186 A) whose output was recorded using a time constant of 10 sec. The PA spectra of sample were normalized using the PA signal from carbon black recorded under identical experimental condition.

3. Result and discussion

The photoacoustic spectra of Nd and Er ions doped in calibo glass have been recorded in the visible region and are shown in Figures 1 and 2. The assignments of the peaks in the spectrum have been made on the basis of the earlier absorption, fluorescence and photoacoustic spectra of the respective ions either in the free state or in other compound [7-9]. These assignments have been shown in Tables 1 and 2. Earlier, we have recorded the PA spectra of rare-earth ion in oxide and compound of rare-earth ions in organic and inorganic compounds [10]. The PA spectra of Nd and Er doped glasses exhibit a large number of peaks. These peaks are due to triply ionized rare-earth atom shifted slightly from their free ion positions due to host lattice. The peaks due to rare-earth ions in the glasses exhibit a red-shift as compared to the corresponding rare-earth oxides. This red-shift has been termed as the nephelauxetic effect by Schaffer [11] and has been discussed in detail by Jorgenson [12]. In

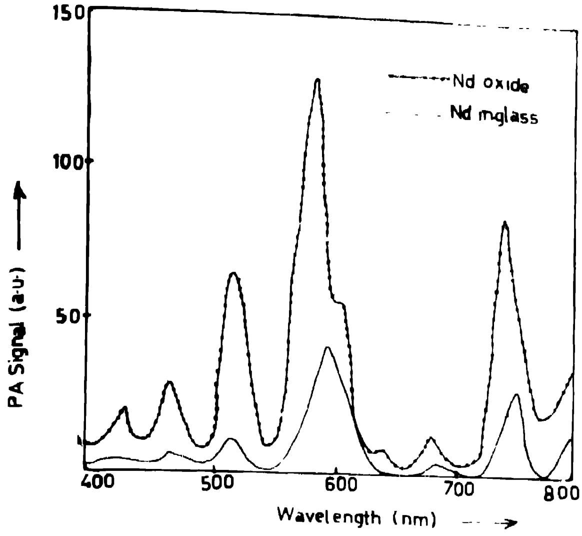

Figure 1. PA spectra of Nd doped in calibo glass

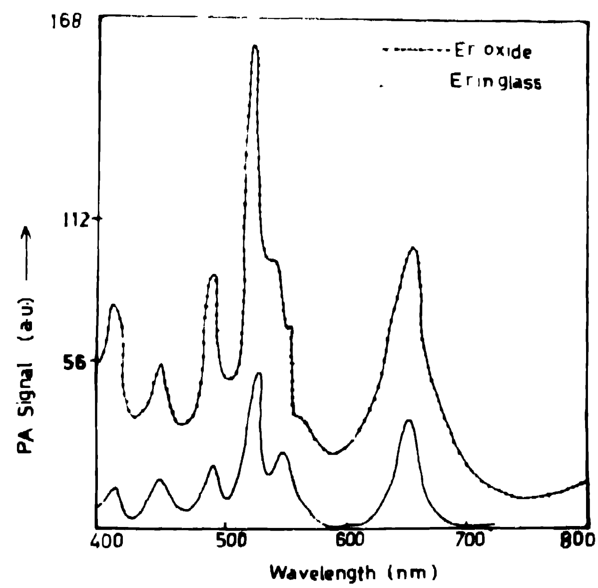

Figure 2. PA spectra of Er doped in calibo glass

this paper, we have defined quantitatively a parameter β which is equal to the ratio of electron repulsion parameters in the glass and the free ion. In general, it is defined as the ratio of

Slater's integrals F_k or Racoh parameters E^k such that $\beta = (E^k)_g/(E^k)_f$. In our measurements, the free ion data have been taken from reference [9] and hence the β values can be calculated as given in Tables 1 and 2.

Table 1. Assignment of peak of Nd in oxide and calibo glasses ground state $\left({}^4I_{9/2}\right)$.

Level assignment	Observed PA in oxide	Observed PA in glass	Relative intensity (a.u.)		Energy of the peak in free ion (cm^{-1})	Energy of the peak in glass (cm^{-1})	β
			oxide	glass			
${}^2P_{1/2}$	430						
${}^4G_{11/2}$	465	465	60	12	21650	21505	0.993
${}^2G_{9/2}$	515	520	128	21	21300	19230	0 902
${}^4G_{9/2}$	580	590	261	84	19560	16949	0.866
${}^2H_{11/2}$	640						
${}^4G_{9/2}$	680	685	14	8	14700	14598	0.993
${}^4F_{7/2}$	740	750	169	58	13500	13333	0 987

Table 2. Assignment of peak of Er in oxide and calibo glasses ground state ${}^4I_{15/2}$

Level assignment	Observed PA peaks in oxide (nm)	Observed PA peaks in glasses (nm)	Relative intensity (a.u.)		Energy of the peak in free ion (cm^{-1})	Energy of the peak in glass (cm^{-1})	β
			oxide	glass			
${}^2G_{9/2}$	410	415	145	24	24475	24399	0 977
${}^4G_{5/2}$	450	450	108	31	22454	22222	0.989
	490	490	168	41	20494	20408	0 995
${}^2H_{11/2}$	520	530	318	102	19011	18518	0 974
	540						
${}^4S_{3/2}$	555	550			18300	18181	0.993
${}^4G_{9/2}$	650	650	182	71	15183	15267	1.005

The relative intensities of the peaks in the PA spectrum are different from that in the oxide form. In order to characterize the change in intensity of the PA transition, Strek *et al* [3] have defined the PA branching vector Y^{PA} which corresponds to the ratio of the integrated intensity of one of the peak in the spectrum to the total intensity of all peaks *i.e.*

$$Y_k^{PA} = I_k^{PA} \quad \sum_{k=1}^{n} I_k^{PA}$$

The branching ratios thus obtained for the various peaks in the photoacoustic spectrum in glass, have been given in Table 3. It is interesting to note that the branching ratio of Nd and Er in various host materials are very similar, suggesting a similar spectral distribution. An

Table 3. Comparision of relative intensities of PA peaks of Nd and Er doped glasses.

R E	[illegible]		Spectral range and branching ratio of Strek *et al* [3]
	400 – 490	0.14	450 - 490 = 0 11
	490 – 550	0 09	490 – 562 = 0.26
	550 – 630	0 52	562 - 652 = 0 36
	660 – 700	0 02	652 – 700 = 0 05
	720 – 775	0.22	700 - 788 = 0 22
	400 – 428	0.27	
	428 – 470	0 09	450 – 510 = 0 25
	470 – 500	0.10	510 - 562 = 0 43
	500 – 600	0 42	562 – 612 = 0 10
	600 – 700	0 31	612 – 710 = 0.23

inspection of the data tabulated in Table 3 indicates that PA branching ratio of the relative intensities are approximately similar to Strek *et al* [3] in penta-phosphate crystal. The peaks due to ${}^4F_{3/2} \leftarrow {}^4I_{9/2}$, ${}^4I_{11/2} \leftarrow {}^4I_{13/2}$ transitions of Nd and ${}^4S_{3/2} \leftarrow {}^4I_{9/2}$, ${}^4I_{11/2} \leftarrow {}^4I_{13/2}$ transitions in Er lead to laser action in the visible region and data of PA branching ratio defined here, may be useful in understanding the mechanism of laser action.

4. Conclusion

In this paper, we have reported the PA spectrum of Nd and Er doped in calibo glass as a quantitative measure of PA intensity of f-f transition bands. The intensity branching vector is proposed. It is clear from the data, that the spectral feature arising from levels with large non-radiative transition probability have a strong PA signal. It shows experimentally that the PA signal is large if the radiative lifetime of the state is very large. The observed PA signal at 430 nm and 450 nm originating from ${}^2P_{1/2}$ and ${}^4G_{11/2}$ level of Nd^{3+} is very very weak in calibo glass, suggesting the non-radiative de-excitations at these wavelengths are very small. The intensity of the radiative absorption at 450, and 430 nm in Nd^{3+} doped calibo glass is very large. This suggests that Nd^{3+} doped in calibo glass may be used as lasing material for wavelength near 450 and 430 nm.

Acknowledgments

This work was done at the Laser and Spectroscopy Laboratory, Banaras Hindu University, Varanasi (India). The helpful discussion with Prof. S N Thakur are gratefully acknowledged.

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